2017 OTCO Laboratory Analyst Workshop

Purge and Trap Theory And Troubleshooting

Columbus, OH

EST analytical Solutions Group

EST analytical

Corporate Headquarters in Cincinnati, OH.

Established in 1990 as instrument distributor with sales and service responsibilities.

Began manufacturing EST VOC products in 1999.

Products designed for high throughput environmental VOC applications.

Service professionals come from environmental laboratory backgrounds.

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OTCO Training Course

Background Training

Purge and Trap

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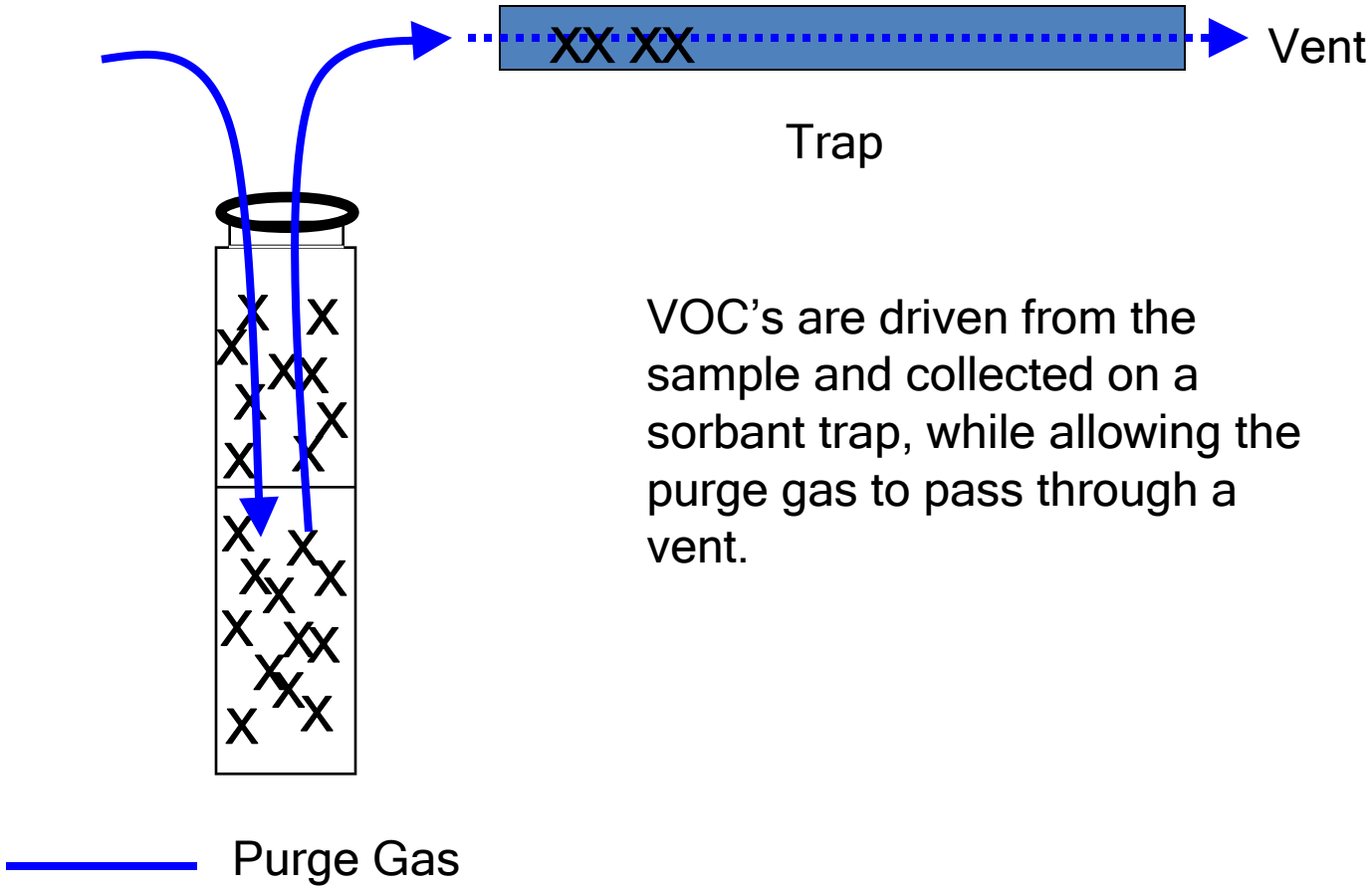
What is Purge and Trap?

Analytical sample preparation technique for GC and GCMS analysis.

Inert gas is passed through an aqueous sample to extract insoluble volatile organic compounds that are collected on a trap.

The trapped analytes are then injected to the GC inlet by heating of the trap while in line with the inlet carrier gas stream.

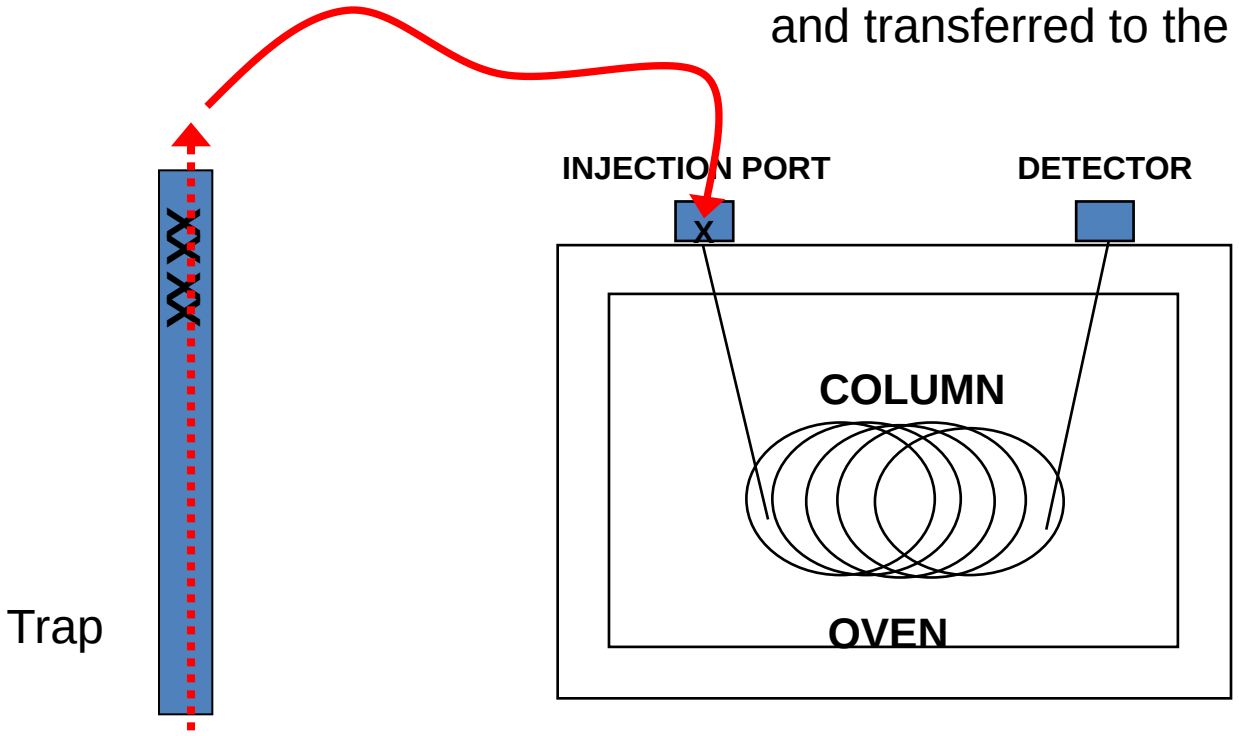
Basic Operation – Step 1



VOC's are driven from the sample and collected on a sorbant trap, while allowing the purge gas to pass through a vent.

Basic Operation – Step 2

The trap is heated and the VOC's are backflushed off the trap by the carrier gas and transferred to the GC.



Definition of VOC

A volatile organic compound (VOC) is any compound that has a boiling point below 180 deg C.

- Preferred qualities for Purge and Trap (P/T)
  - Low boiling point
  - Insoluble or slightly soluble in water

VOC Examples

Dichlorodifluoromethane

Benzene

Xylene

Toluene

Naphthalene

Note: Analytes meet preferred qualities.

Why Purge and Trap?

Increased Sensitivity

- Provides a means to deliver increased mass quantities of VOC's onto a GC column. "Concentration of VOC's"

Inability of GC Applications to tolerate water injections.

- Many columns and detectors are adversely affected by the presence of water.

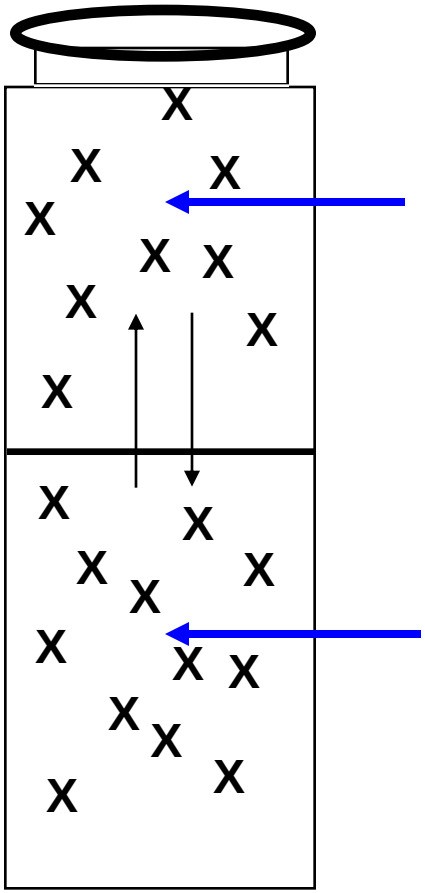
Delivers sample in a vapor form.

Basic Science of PT

- The technique of analyzing water and soil samples by purge and trap is based on the concept of headspace equilibrium
- The continual disruption (“sweeping”) of the headspace leads to the extraction of the VOC analytes from the sample for analysis by GC and GCMS.

Headspace Equilibrium

Headspace is defined as the vapor space above a sample.



VOC's, given time, will migrate out of the sample and into the headspace until an equilibrium is established.

In other words, headspace equilibrium is the result of equal concentrations of VOC's in the sample and the headspace.

Gas Extraction

Purge and trap sample analysis is actually a gas extraction, rather than a static headspace technique described by headspace equilibrium.

Gas extraction refers to the process of continually sweeping the headspace with an inert gas, thus reducing the vapor pressure above the sample.

The reduction in vapor pressure above the sample encourages the migration of VOC's into the vapor phase while eliminating migration from vapor phase to the liquid phase.

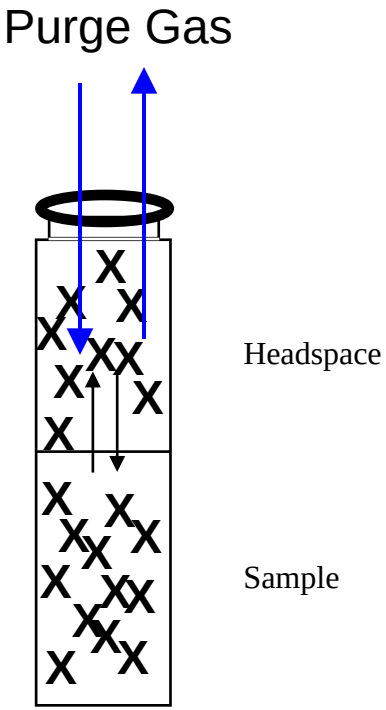
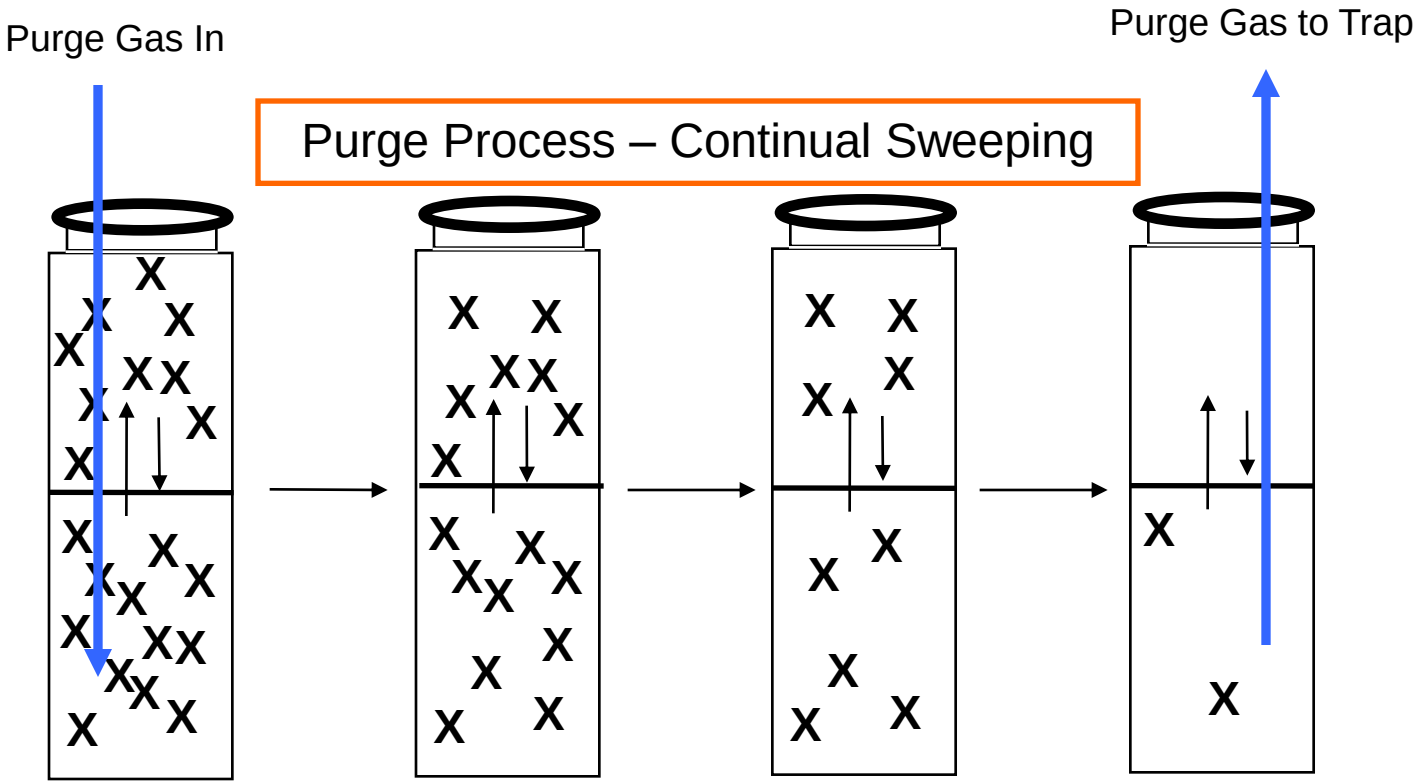


Illustration of Gas Extraction



Purge Efficiency

Many factors determine how well the VOC's are removed from the water or sample matrix. We will now review these factors that effect the ability of the VOC analyte to transfer from the liquid phase to the gas phase.

Purge Efficiency = The percentage of VOC's transferred from the liquid phase to the vapor phase through the gas extraction process.

Factors Determining Purge Efficiency

Vapor Pressure

Solubility

Temperature

Sample Size

Purge Volume

Type of Purge Method

Effects of Vapor Pressure

The greater the vapor pressure the greater the purge efficiency.

High vapor pressure analytes migrate into the vapor phase rapidly due to their preference to exist in a vapor state.

- Example – Dichlorodifluoromethane – high purge efficiency.

Effects of Solubility

The greater the solubility in the sample matrix, the lower the purge efficiency.

- Example: Methanol is very soluble in water and the purge efficiency is about 10%. This is the primary reason most VOC stds are prepared in methanolic solutions.

Effects of Temperature

The higher the purge temperature, the greater the purge efficiency.

- Increasing the purge temperature, increases the vapor pressure of the VOC's in the sample matrix. (See Effects of Vapor Pressure)
    - Note: For each 10 deg C rise in purge temperature, the amount of water transferred doubles.

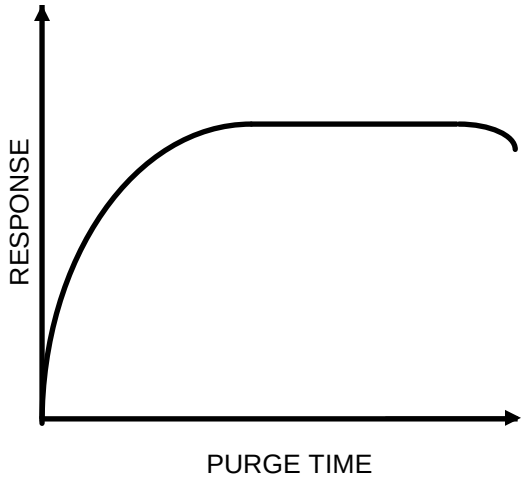
Effects of Purge Volume

- Defined as the total volume of gas used to purge a sample.

Increasing the purge volume, increases the purge efficiency.

- Purge for 11 min at 40ml/min = 440 ml purge vol

Note: When increasing purge volume, a point is reached where the efficiency gain is insignificant and time required becomes too lengthy.



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Effects of Sample Size

Increasing sample size actually reduces purge efficiency.

- Large sample volumes require more purge volume to achieve equivalent purge efficiencies to standard sample volumes.

Note: Sensitivity is increased due to increased ng of VOC's transferred.

Example: 5 ppb std

5 ml sample size = 25 ng on column

25 ml sample size = 125 ng on column

Equivalent purge volumes result in a 70 to 80% increase in sensitivity with 100% increase in sample size.

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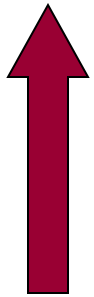
Effect of Purge Method

- Frit Sparger
- Fritless Sparger
- Needle Sparger



Purge Efficiency

Increasing the amount of purge gas which comes into contact with the sample increases purge efficiency.

Review of Purge Efficiency

- Vapor Pressure – High pressure increases efficiency.
- Solubility – Higher solubility decreases efficiency.
- Temperature – Higher temperature increases efficiency – but also increases water transfer.
- Purge Volume – more purge gas increases efficiency
- Sample Size – Greater sample size reduces efficiency if purge volume stays the same.
- Purge Method – Frit sparger is the best technique for the highest efficiency.

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Equipment Overview

The “System”

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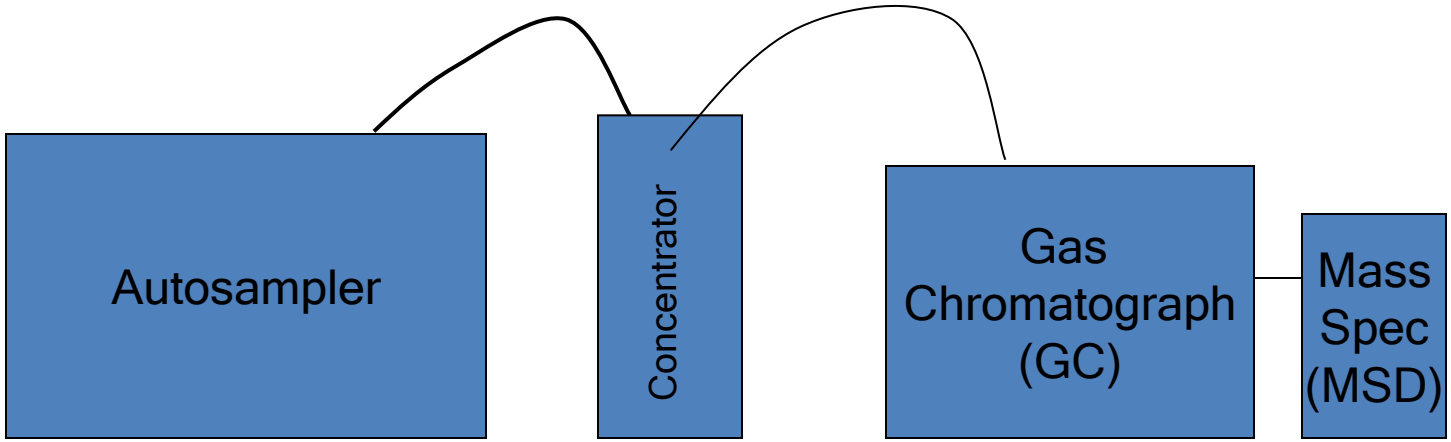
System Configuration



A purge and trap "system" is made up of the following components:

Autosampler (Optional)

Concentrator

GC

MSD (Optional)

Required Interfaces:

Transfer Lines

Interface Cables

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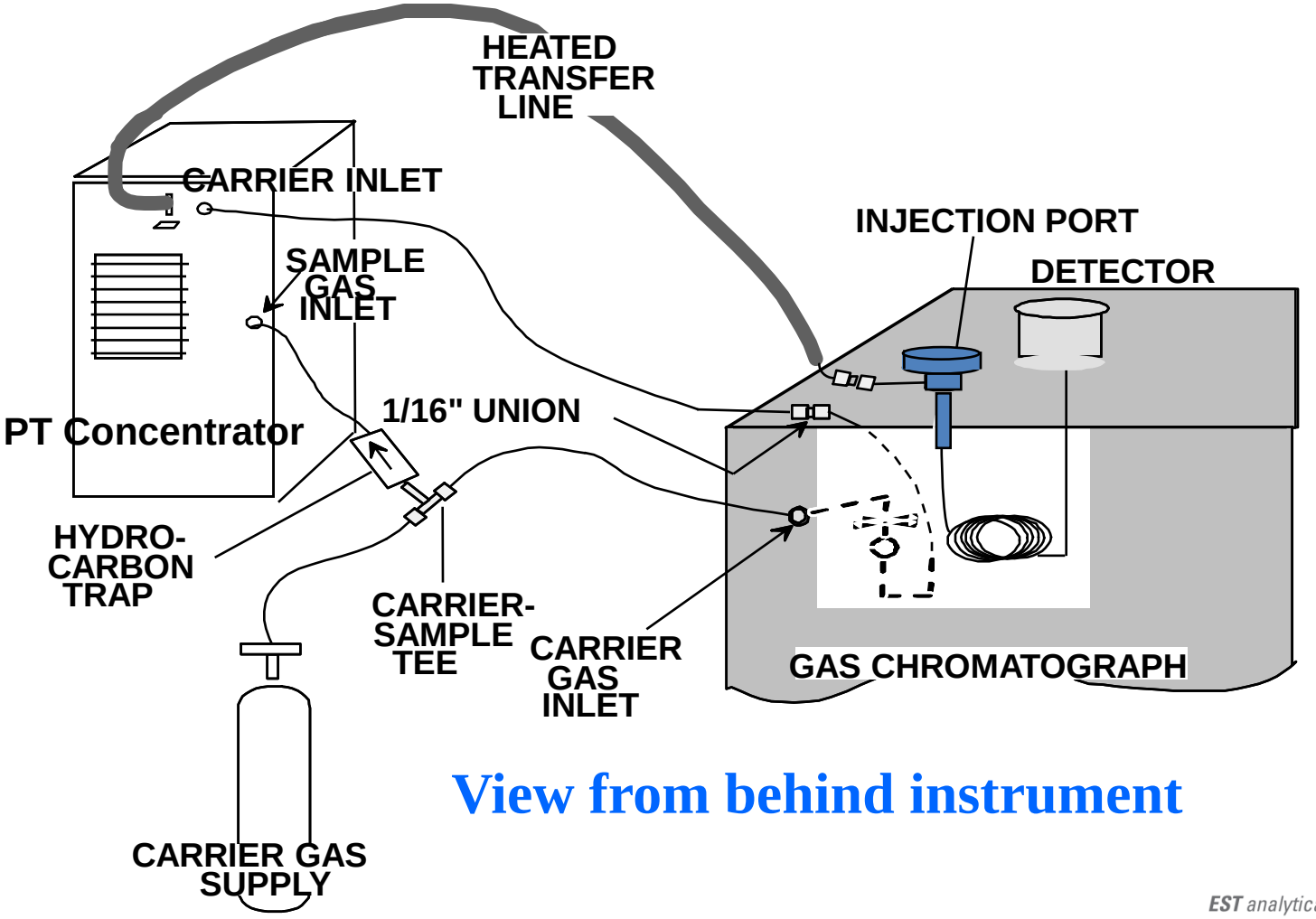
Configuration – GC and/or GCMS



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Maintenance
and Troubleshooting

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P/T Troubleshooting

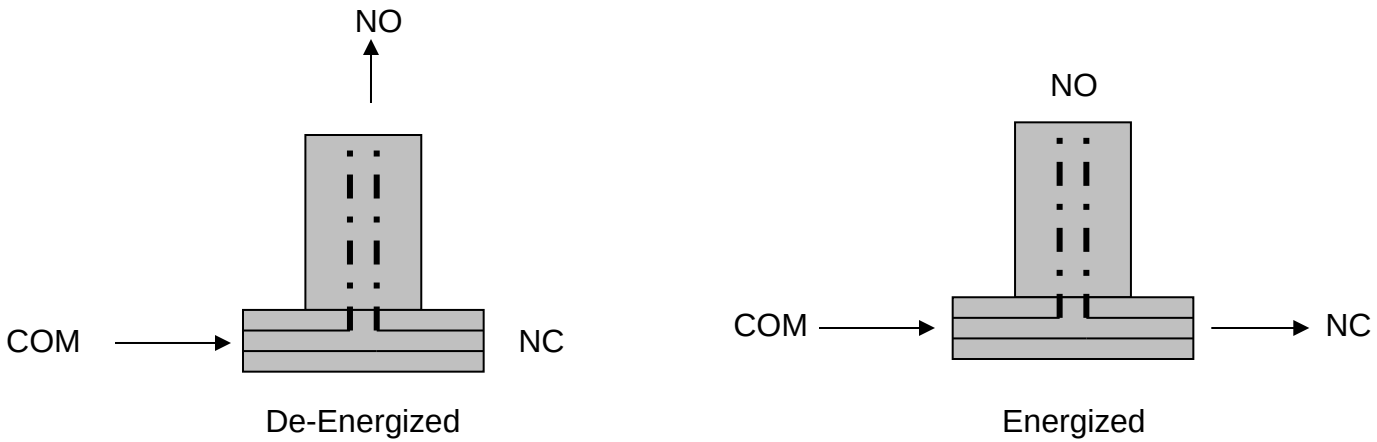
Any and all VOC instrument troubleshooting

should begin with a lesson in reading flow diagrams.

- Valve types utilized in P/T Concentrators
  - Manifold System; “Gatekeepers”
  - 2 Port and 3 Port Valves (24V DC)
  - 6 Port Rotary Valve and 8-Port Rotary Valves

P/T Troubleshooting

Standard 3 Port Solenoid Valve Configurations



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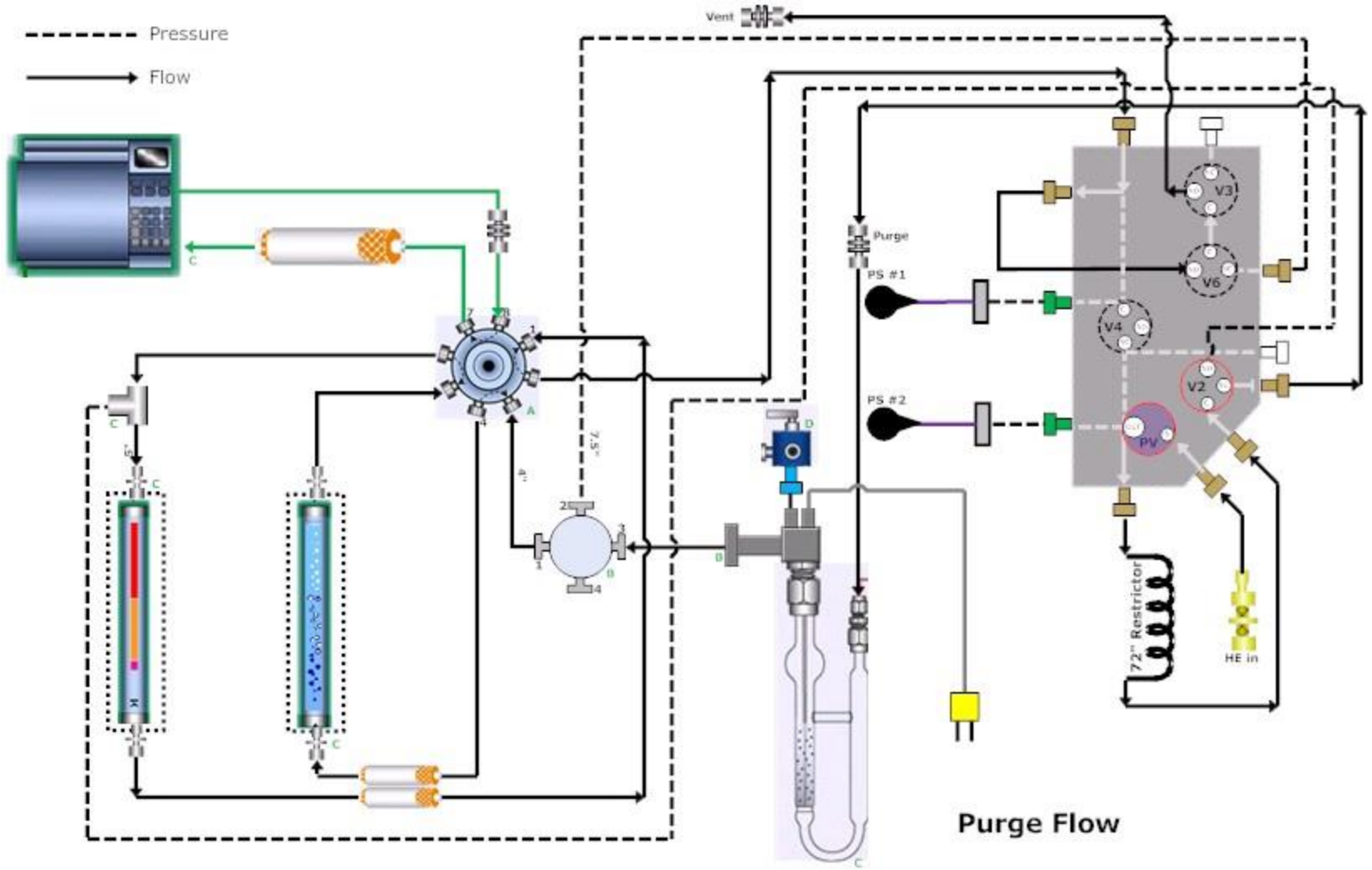
Basic Operation – Purge



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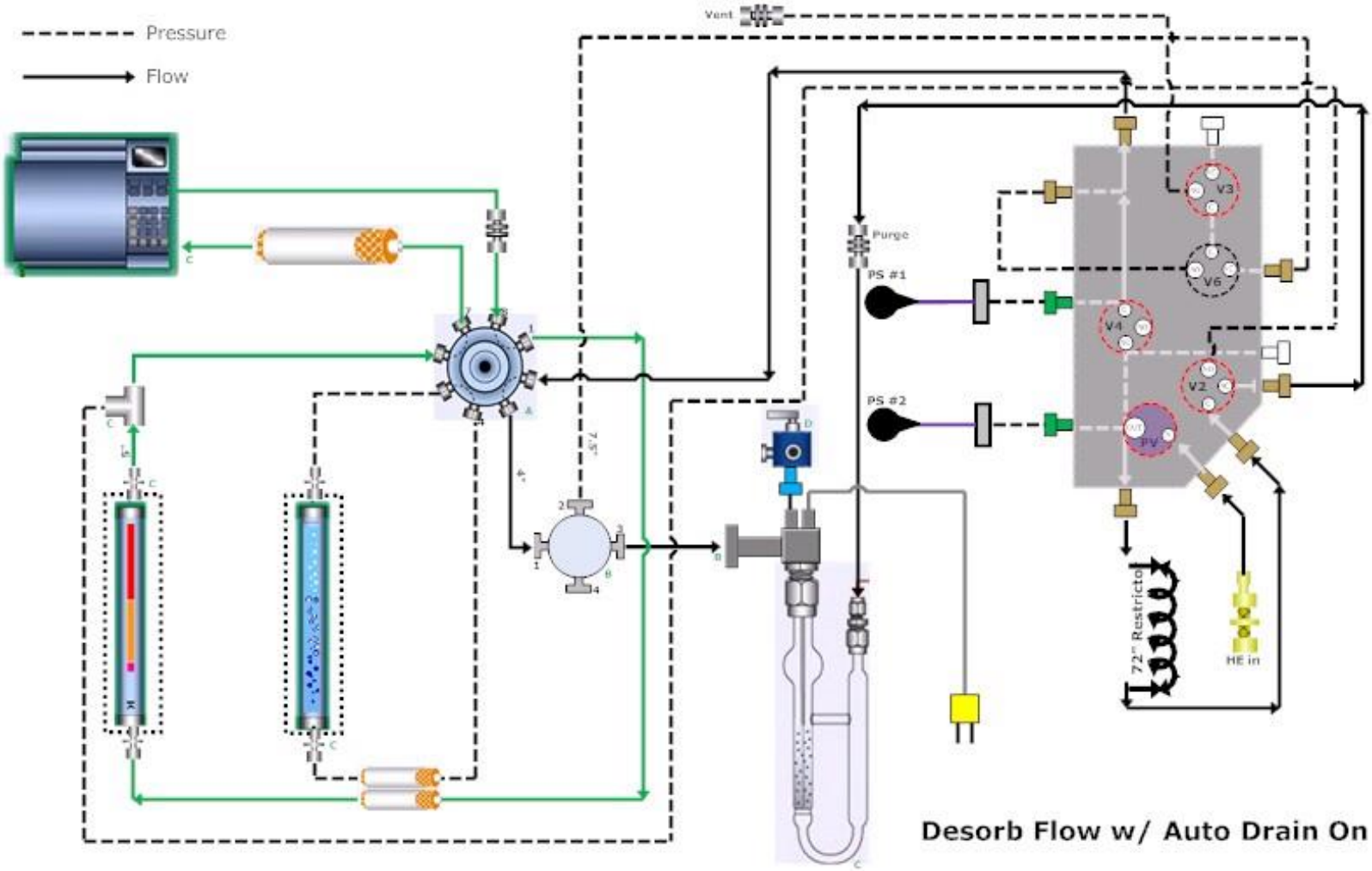
Basic Operation - Desorb



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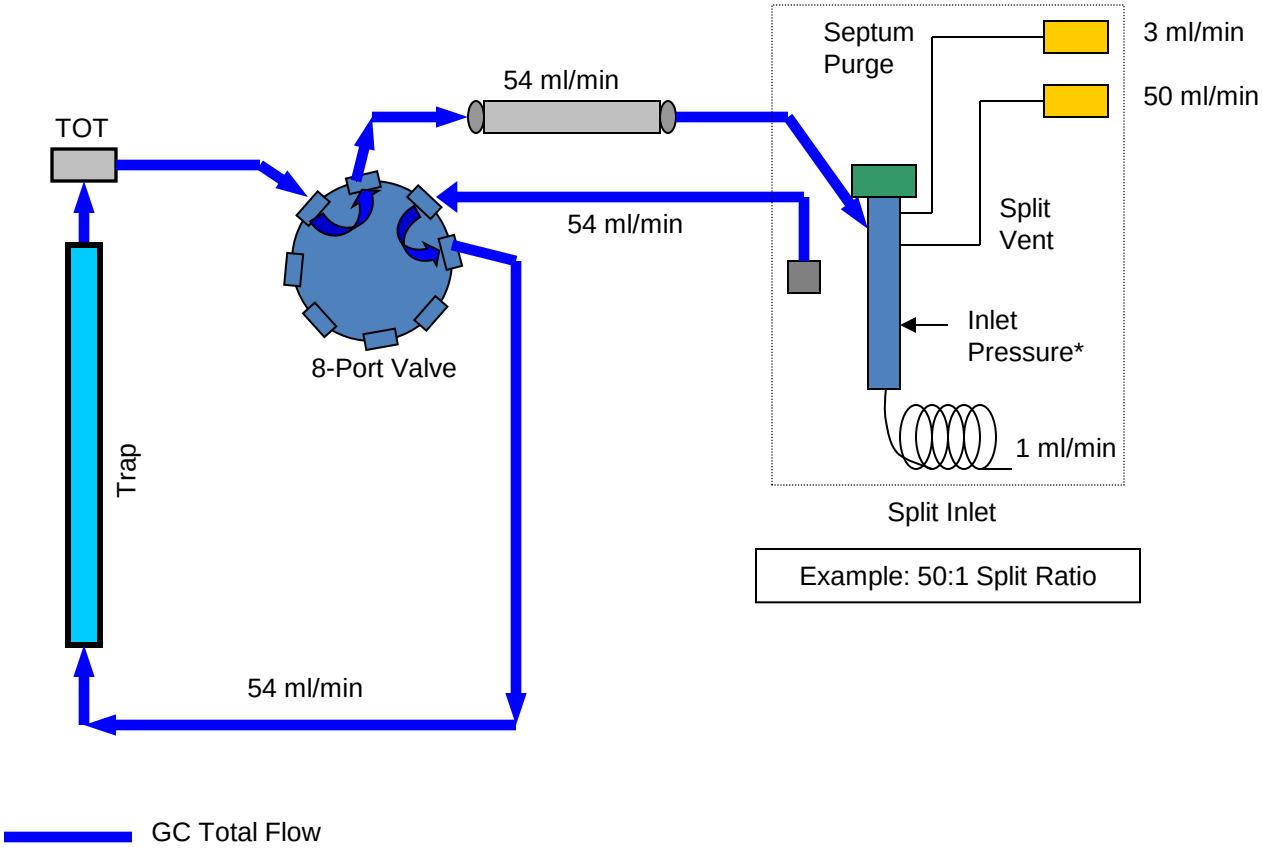
P/T Concentrator Desorb Mode
Detailed Flow Diagram – 8 Port Valve Design



Note 1: * = Inlet head pressure based on column size and desired column flow rate.

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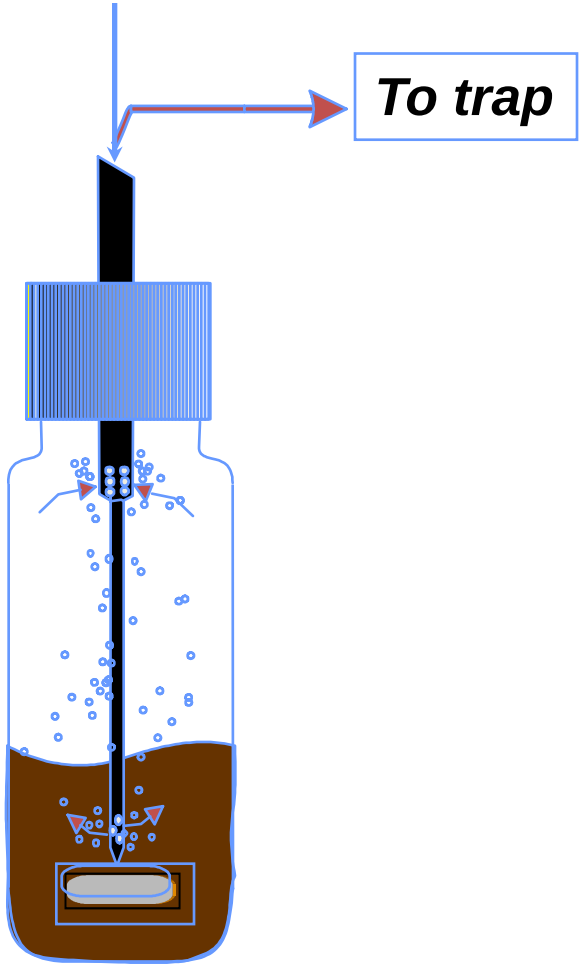
Common Problems with P/T Analysis

- Water Management
  - Causes loss of response – drop off
- Inconsistent Results
- Contamination / carryover
- Loss of Response
  - Flow issues
  - Leaks
  - Restrictions

Why Control Moisture?

- During purging process water is also removed from sample
  - Water itself does not create problems within the Purge and Trap Concentrator.
  - Does create Problems with GC Detector systems and GC/MS systems
- **Water is a major Issue with EPA Method 524.2 (4 min Desorb times)**



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Water in GC/MS

- Creates Interferences which causes unstable areas with the early eluters.
- Can observe water Band eluting from column by a large baseline rise.
- May even cause MS to shut down with an excessive source pressure error message.
- Drop in response over a 12-hour “tune” period caused by water buildup.

How to Control the Water?

- Use Condensation Traps
- Use the Dry Purge Step
- Desorb Parameters
  - GC split ratio
  - Time
- Bake Parameters
  - High Flow

Using the EST Evolution to manage the water transferred

EST Encon Evolution

- Condensation
  - Moisture Reduction Trap (MORT)
- Dry Purge
- Desorb Flow control

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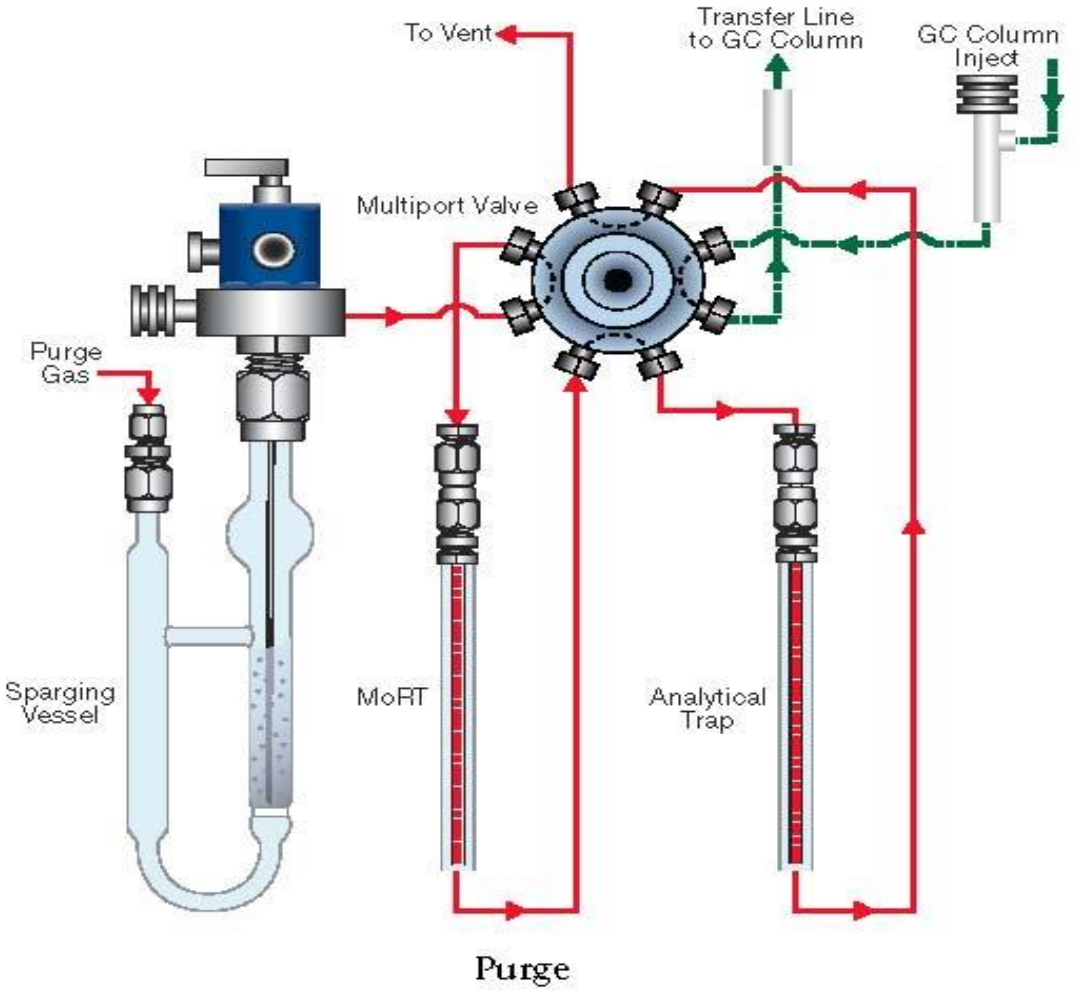
MoRT – Moisture Reduction Trap

- Water management performed during the purging process
  - During the purge cycle the water management system is ambient to allow the water to condense before reaching the adsorbent trap
- Makes the Analytical Trap more efficient
- Standard Water Management Parameter

MoRT -- Forward not Behind



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MoRT – Moisture Reduction Trap

- During the Desorbing process the water which has been condensed in the MoRT is excluded from the transfer of compounds from the trap to the GC.
  - 8-port Valve

- Minimizes Dead Volume and Cold Zones during the critical transfer of compounds from the trap to the GC.
  - Superior Chromatography

Best Practice – Solving Inconsistent Results

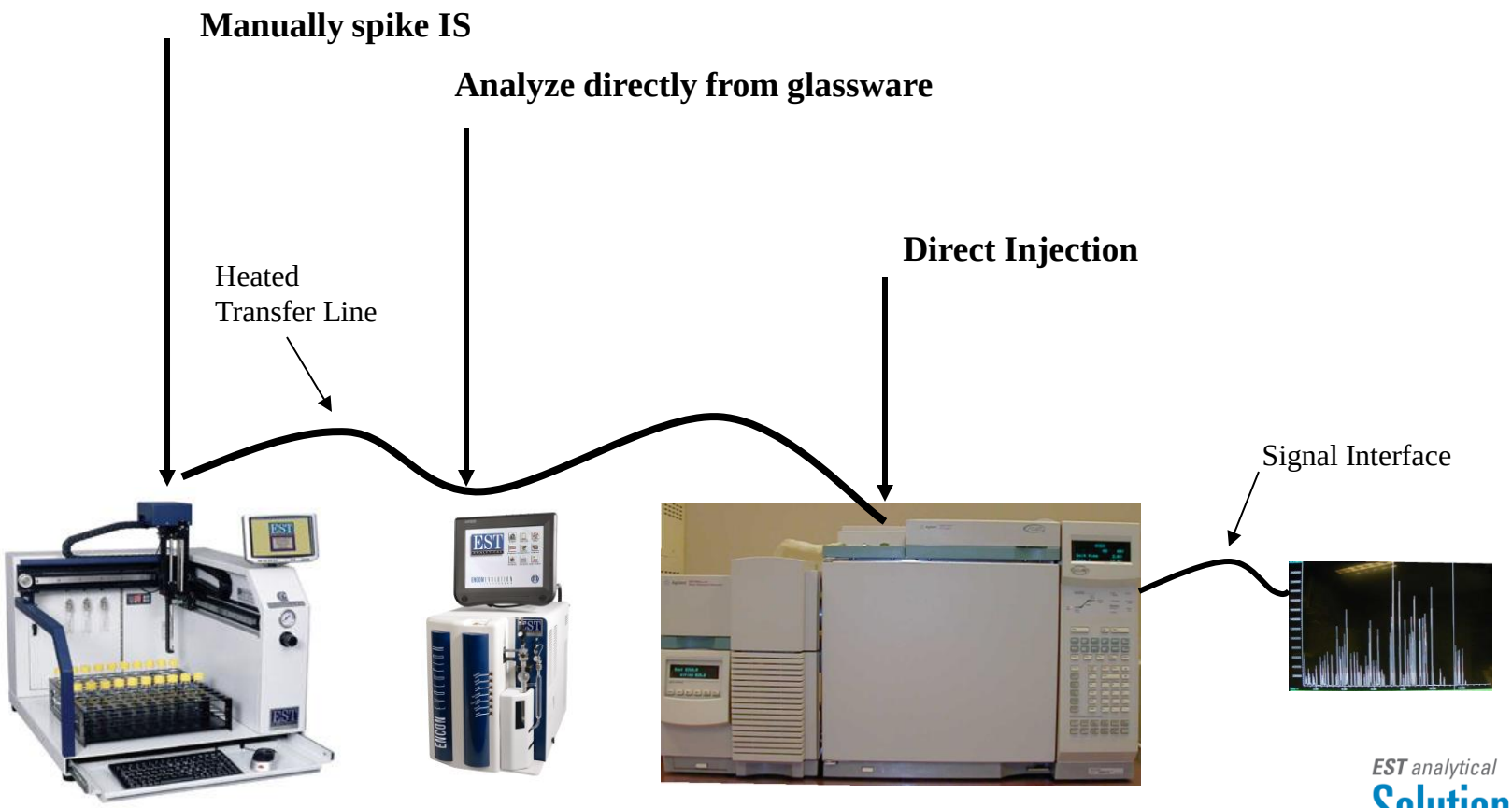
Use of **Halfsplitting** Techniques to solve P&T Problems

- As the name suggests - Purge and Trap analysis is a Multi - Dimensional Method.
  - Halfsplitting is a powerful troubleshooting technique which makes problems such as system activity, contamination and response variability easier to diagnose when variables are reduced.

Halfsplitting

Halfsplitting refers to the process of removing variables from a system in order to more accurately determine the source of a problem.

Example: Halfsplitting for inconsistent IS response or analyte response



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How to decrease the Carry-Over

- Low surface area
  - Small number of parts that the sample contacts both during purge and desorb.
  - Efficient glassware cleaning and rinsing during bake.
    - Autosampler Rinsing Trick – 1 ml additional rinse volume.
    - Avoid large volume glassware for 5 ml purge samples. Condensation.
- Patent pending bake parameters – EST Analytical
  - Heating Glassware during bake along with hot water rinsing prior to bake cycle.

Carry Over Virtually Eliminated

- Heating of the Glassware
  - Most of the carryover seen in a purge and trap actually comes from the glassware
  - During Bake, you can now program a parameter to heat the glassware up to 110^0C during the rising process with water

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Carry Over Virtually Eliminated

Percent Carry Over	1st Blank	2nd Blank
Benzene	ND	ND
Toluene	ND	ND
Ethylbenzene	ND	ND
Xylene (m+p)	ND	ND
1,2,4-TCB	0.25	ND
Napthalene	0.21	ND
Hexachlorobutadiene	0.21	ND
1,2,3-TCB	0.25	ND

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Halfsplitting to determine source of Contamination and Carryover

- Step Concentrator to Desorb Preheat and collect data without purging.
  - If peaks of concern appear in Chromatogram then Desorb pathway is the culprit.
    - Most likely insufficient removal of compounds from trap during Bake Cycle.

Resolution to Problem in Desorb Pathway

- Bake trap longer between samples.
  - Long Bake times do not shorten life of trap. The incomplete removal of compounds is what actually shortens trap life.
    - If problem persists replace trap or GC Transfer Line is contaminated.

Resolution to Problem when isolated to Sample Pathway

- Two Categories of Sample Pathway Contamination.
  - Vapor Phase Adsorption
  - Liquid Phase Deposition

Vapor Phase Adsorption

- **HOT SAMPLE**

- Occurs when high concentrations of a compound in the sample gas phase passes over an Adsorptive surface.
  - Polymer Surface
    - 6-port valve rotor
  - Nickel Tubing lines in sample pathway.

Recovering from Contamination in the Sample Pathway

- Vapor Phase Adsorption can usually be recovered from by a **Thermal Bake Out**
  - Elevate the valve, mount and line temperatures of the Purge and Trap with clean sample gas flowing through the pathway.

Liquid Phase Deposition

- Worst kind of contamination!
- Occurs when the liquid sample is carried by the sample gas into the heated zones and lines while purging. Commonly known as *"FOAMERS"*
  - **Contamination is the result of these foreign materials outgassing or decomposing into additional compounds. May even act as active sites to absorb compounds.**

Replace Sample Pathway

- Mount
- All Sample Tubing
- Top of Trap Fitting
- 8-Port Valve
- Trap
- Dry purge TEE

Proper Leak and Flow Checks

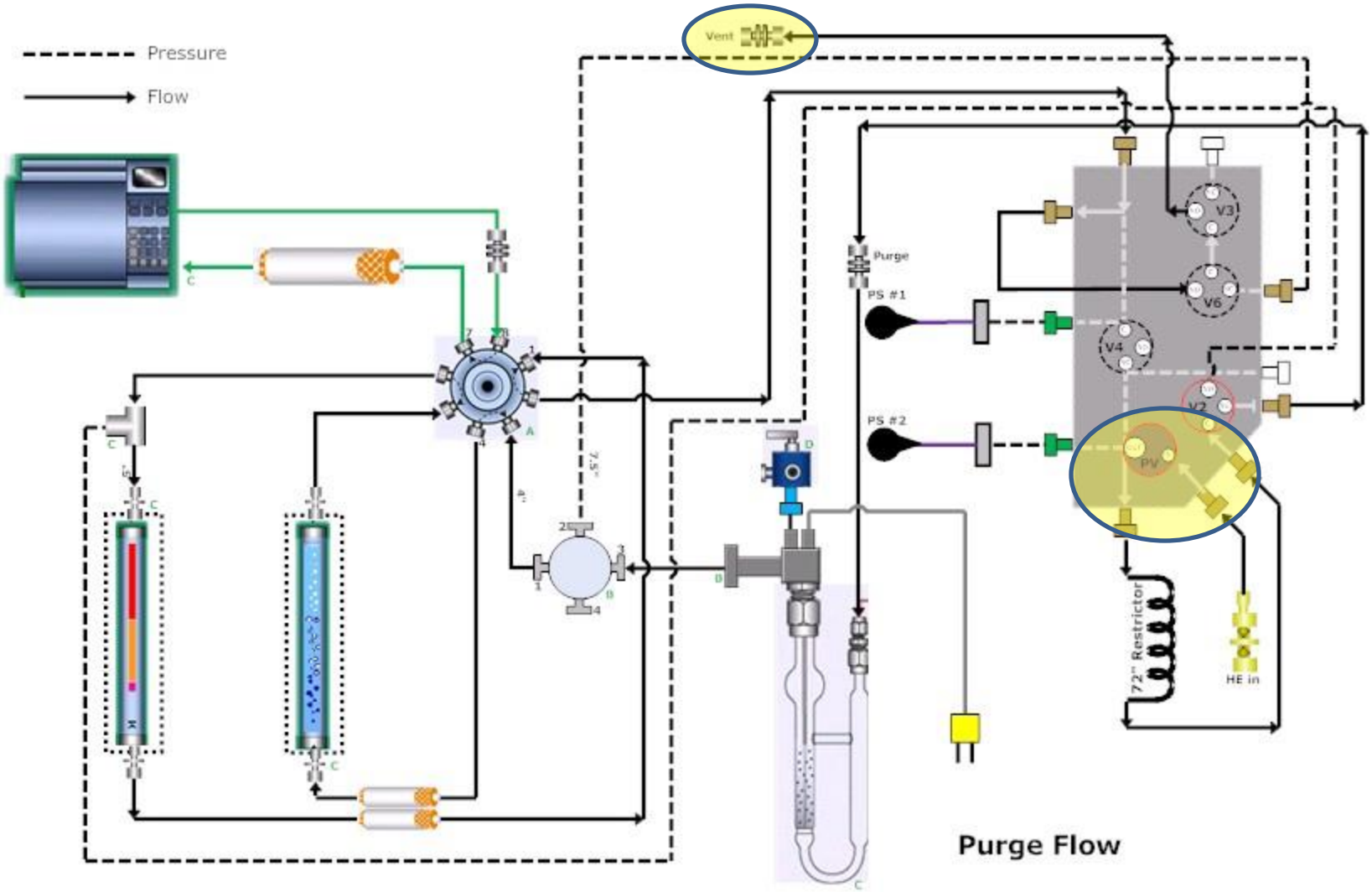
- Beyond managing water and carryover, dealing with leaks and flow issues are among the biggest challenges associated with Purge and Trap analysis.
- When diagnosing P/T problems related to response and consistency, a properly performed leak check can be invaluable. Assists halfsplitting the P/T System.
- Constants for P/T systems:
    - Generally operate at 20 psi.
    - Purge flow at 40 ml/min.
    - Flow at vent during purge should be within 5 ml/min with nominal backpressure.

Reduced Response for all Compounds

- Usually indicates there is a **LEAK.**
- Perform a Pressure Decay Leak Test

Newer systems with EPC and Mass flow controllers have built in leak check algorithms.

Basic Operation – Leak Check



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Restrictions

- Compare Purge Flow at the Input and the Vent.
  - Should be close to equal. *IF NOT*
- Verify that the system is leak free.
  - *IF NO LEAKS*
- Measure flows systematically in a backtracking fashion to isolate portions of the pathway to determine the restricted component.
  - Replace component or remove restriction

Activity

- Specific classes of compounds may show reduced response:
  - Brominated Compounds
    - Bromoform
- Other compounds susceptible to active sites may disappear or deliver poor linearity.
  - 2-Chloroethyl vinyl ether
  - Naphthalene – quadratic calibration

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